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Characterizing and Modeling Physical Aging in Polymeric Composites

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**14. ABSTRACT**
Physical aging in polymeric composites was experimentally investigated and analytically modeled. Attention was focused on physical aging behavior on elastic and creep compliances. Short term creep tests were conducted under isothermal conditions on off-axis composite specimens for different temperatures as well as moisture contents. A master creep curve was employed to describe the anisotropic creep behavior in the composite with the aid of a one-parameter creep potential function. Shift factors and shift rates were used to collapse the creep curves of different aging times to a chosen reference creep curve. An effective time was introduced to predict the long term creep compliance based on the creep model established based on the short term creep data. Moisture has a similar effect on the rate of physical aging. In the present study, a temperature-moisture equivalence was established for the effects of these two variables. With this equivalence, the effect of moisture on physical aging can be predicted using the model with temperature.

**15. SUBJECT TERMS**
polymeric composites, physical aging, temperature, moisture, glass transition temperature, creep compliance, elastic compliance, effective time, composite laminates

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**SUMMARY**

Polymer matrix composites have been widely used in aircraft structures. One common aspect shared by structural designers is the concern of long-term durability especially for potential changes in mechanical and physical properties over time under the exposure to elevated temperatures and other environmental conditions. One of the key mechanisms causing these changes is physical aging, which is a process occurring below the glass transition temperature ($T_g$) of the matrix. Theoretically, physical aging continues indefinitely as long as the service life of the composite structure. The objective of this research was to understand and to model physical aging in order to assess the long-term durability of polymeric composites.

Physical aging affects elastic and creep compliances. In this study, these effects were observed and modeled separately. Short time creep tests were conducted to obtain data for modeling the effects of physical aging on elastic and creep compliances. An effective time concept was introduced to predict the long-term creep based on the momentary (short term) creep compliance model. This approach was successfully demonstrated in a long term creep compliance test that lasted up to 100 times of the short term aging time used in establishing the creep model.

Effective creep compliance model was developed to characterize physical aging in orthotropic composites. By using a one-parameter creep potential function, momentary creep compliances with different fiber orientations were collapsed into a single master curve. The master curve can be used to describe the creep behavior in any direction of the composite.

Moisture and temperature can relax the elastic and creep compliances throughout the period of physical aging. In this study a moisture-temperature equivalence in physical aging for elastic and creep compliances was established. These equivalence enables us to interchange the effects of moisture and temperature on physical aging in polymeric composites.

The validity of laminate theory in characterizing physical aging of elastic compliance in composite laminates has been experimentally verified.

**OBJECTIVES**

Polymer-matrix-dominated mechanical and physical properties change significantly over time due to exposure to elevated temperatures and humid environments. One of the mechanisms causing these changes is physical aging, which is a process occurring below the glass transition temperature ($T_g$) of the matrix [1]. Theoretically, physical aging continues indefinitely as long as the service life of the composite structure. Therefore, it is essential to understand and to model physical aging in order to assess the long-term durability of polymeric composites. The objective and scope of this research include the following

- Characterize physical aging in elastic and creep compliances of polymeric composite respectively - Short-term creep test data were used to predict the long-term creep behavior under isothermal aging.

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- Develop a model to account for physical aging in polymeric composites with different fiber orientations - An effective creep compliance model to express the creep compliances in different off-axis specimens under aging was developed.
- Establish an equivalence of moisture and temperature effects in physical aging so that we can interchange these two effects in physical aging.
- Characterize physical aging in composite laminates - The application of classical laminate theory to aging-dependent mechanical properties of polymeric composite was investigated.

## APPROACHES AND ACCOMPLISHMENTS

*Creep compliance test:* Prior to creep test, the specimen was rejuvenated up to 205°C for 5 minutes and was rapidly cooled down to the test temperature by using high-pressure air. After rejuvenation, the specimen was aged at the constant temperature for several aging cycles, for example, 5, 12, 24, 48, 72 and 96 hours. At the end of each cycle, a momentary creep test was performed. The momentary creep test was conducted for a time less than 1/10 previous aging time. Applied loads were kept small enough so that material was in its linear viscoelastic behavior.

*Physical aging in elastic compliance and creep complianc:* The experimental data shown in Figure 1 indicated that elastic compliance decreases as aging time increases and seems to approach a steady state value at long-term aging. The experimental data for all off-axis specimens were fitted into an exponential function as [2]

$$S_x^e = S_x^0 / (1 - \alpha e^{-\gamma t}) \qquad (1)$$

where $S_x^0$ is the steady state elastic compliance in the loading direction; and $\alpha$ and $\gamma$ are constants.

Momentary creep compliances shown in Figure 2 decrease as aging time increases. Individual momentary creep compliance was fitted by a power law and can be shifted to a reference curve by using aging shift factors, $m$ and $n$, i.e.,

$$S_{x,ref}^c(t) = (\frac{t}{\tau_{ref}})^{\beta_{ref}} = (\frac{t}{m\tau})^{n\beta} \qquad (2)$$

where $t$ is creep time (hour), $\tau$ is relaxation time (hour), $\beta$ is a shape factor, subscript *ref* refer to a reference state of aging time. Shift factor $m$ and $n$ can be represented as

$$m = (\frac{t_{a,ref}}{t_a})^{\mu_m} \qquad \text{and} \qquad n = (\frac{t_a}{t_{a,ref}})^{\mu_n} \qquad (3)$$

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where $\mu_m$ and $\mu_n$ are aging shift rates, the linear slopes between shift factors and aging time in log-log scale as shown in Figure 4. Using the reference curve and shift rates, we can predict the momentary creep compliance in any given aging time.

*Effective time model and long-term creep prediction:* If the loading time of creep test is not short in comparison to the previous aging time, the aging effect that proceeds as the creep test progresses must be accounted for. An effective time model [1] was adapted to the power law model. The shift factors of relaxation time and shape factor at any instant are aging time dependent and can be expressed as

$$m_0(t) = (\frac{t_a^0}{t_a^0 + t})^{\mu_m} \quad \text{and} \quad n_0(t) = (\frac{t_a^0 + t}{t_a^0})^{\mu_n} \tag{4}$$

where $t_a^0$ is the initial aging time. To follow Struik's approach, we first integrate these two shift factors into one shift factor $G_o$ for relaxation time, i.e.,

$$G_0(t) = [m_0(t)(\frac{t}{\tau_0})^{(1-n_0(t))}]^{(1/n_0(t))} \tag{5}$$

The effective time can be defined as [1]

$$\lambda = \int_0^t G_0(\xi)d\xi \tag{6}$$

Equation (6) can be solved by numerical method. Replacing the real creep time by effective time, the effective time model was obtained, i.e.,

$$S_x^c(t) = (\frac{\lambda}{\tau_0})^{\beta_0} \tag{7}$$

Equation (7) was used to predict the long-term of 45° specimen at isothermal aging of 148 °C as shown in Figure 4. The initial aging time $t_a^0$ is 5 hours. Effective time model can well-predict the long-term creep up to 500 hours.

*Effective creep compliance model:* By using a creep potential and flow rule, an effective compliance model was developed as [3], i.e.,

$$\overline{S}^c(t) = \frac{\overline{\varepsilon}^c(t)}{\overline{\sigma}} = \frac{\varepsilon_x^c(t)}{\sigma_x} \frac{1}{h^2(\theta)} = \frac{S_x^c(t)}{h^2(\theta)} \tag{8}$$

where $h(\theta) = \sqrt{3/2}(\sin^4\theta + 2a_{66}\sin^2\theta\cos^2\theta)^{1/2}$, $\overline{\sigma}$ is effective stress, $\overline{\varepsilon}^c(t)$ is effective creep strain to be measured, $\sigma_x$ is applied axial stress and $a_{66}$ is the only unknown parameter to be determined experimentally. Using $a_{66} = 0.95$, the creep compliance curves for different off-axis specimens shown in Figure 5 were collapsed into

a single master curve of effective creep compliance as shown in Figure 6. Consequently, master curves for different aging times can be obtained by using $a_{66} = 0.95$.

*Moisture-temperature equivalence in physical aging:* Experimental data shown in Figure 7 indicated that moisture can proportionally increase elastic compliance and the data can be vertically shifted to coincide with other curves with a shift factor $a_M^e$, i.e. [4],

$$S_x^e(t_a, M) = a_M^e S_{x,ref}^e(t_a, M_{ref}) \tag{9}$$

where $S_x^e(t_a, M)$ is the elastic compliance with moisture content $M$; $M_{ref}$ reference to the reference moisture. Replotting the data in Figure 7 in terms of elastic compliance increment versus moisture content, linear relations were obtained as shown in Figure 8. This enables us to predict elastic compliance of any wet material with any moisture content less than 1.3 % from that of the dry material aged at 23 °C.

The similar results were obtained from dry specimen due to temperature effect. Experimental data shown in Figure 9 indicated that temperature can proportionally increase elastic compliance and the data can be vertically shifted to coincide with other curves with a shift factor $a_T^e$, i.e.,

$$S_x^e(t_a, \Psi) = a_T^e S_{x,ref}^e(t_a, \Psi_{ref}) \tag{10}$$

where $S_x^e(t_a, \Psi)$ is the elastic compliance with content $\Psi$; $\Psi = (T - 23^\circ C)/23^\circ C$ is temperature increment (%) and $\Psi_{ref}$ corresponds to the reference temperature. In this study, we chose 23 °C ($\Psi_{ref} = 0$) as the reference temperature. Replotting the data in Figure 9 in terms of elastic compliance increment versus temperature increment, linear relations were obtained as shown in Figure 10. This enables us to predict elastic compliance of the dry material aged in any temperature less than 185 °C from that of the dry material aged at 23 °C. It is noted when temperature reach 193 °C, just a bit higher than $T_g$, the elastic compliance abruptly increased.

If we choose the condition of $M = 0$ and $\Psi = 0$ as a reference state, from equations (9) and (10), an equivalence of moisture-temperature was obtained, i.e.,

$$S_x^e(t_a, M)\big|_{\Psi=0} = S_x^e(t_a, \Psi)\big|_{M=0} \left(\frac{a_M^e}{a_T^e}\right) \tag{11}$$

Equation (11) enables us to interchange the effects of moisture and temperature on physical aging of elastic compliance.

Moisture and temperature can relax the creep compliance. In a given aging time, the increment of creep compliance due to moisture decreases when moisture content increases as shown in Figure 11. By choosing a reference curve in Figure 11, other curves with different moisture contents can be shifted to the reference curve by using a factor

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$a_M^c$. Thus, the relations between logarithmic shift factors and moisture content were fitted in a power law function as shown in Figure 12.

In a given aging time, the increment of creep compliance due to temperature increases when temperature increases as shown in Figure 13. By choosing a reference curve in Figure 13, other curves at different temperature conditions can be shifted to the reference curve by using a factor $a_T^c$. Thus, the relations between logarithmic shift factors and temperature were fitted in a power law function as shown in Figure 14.

By choosing a condition of 23°C and M = 0 % as reference, an equivalence of moisture-temperature in physical aging of creep compliance was obtained, i.e. [5],

$$S_M^c(M,t_a) = (\frac{a_M^c}{a_T^c})^{\beta_* / b_M^c} (S_T^c(T,t_a))^{b_T^c / b_M^c} \qquad (12)$$

In a given moisture content or temperature level but different aging time, the aging shift method can be used predict any momentary creep compliance in any given aging time with a constant moisture content or temperature.

*Physical aging in composite laminates:* Experimental data shown in Figures 15 and Figure 16 indicated that elastic compliances of symmetrical laminates [(+45/-45)$_3$]$_s$ and [90/(+45/-45)$_3$]$_s$ decrease as aging time increases. In laminate [(+45/-45)$_3$]$_s$, constant modulus $E_2$ and $G_{12}$ in laminate theory were replaced by aging-dependent modulus $1/S_{22}$ and $1/S_{66}$. In laminate [90/(+45/-45)$_3$]$_s$, the test data of sub-laminates [(+45/-45)$_3$]$_s$ and [90]$_2$ were used in laminate theory. The results showed that laminate theory provides a well prediction of aging-dependent elastic compliance of laminates.

*Conclusions*: Effects of physical aging on elastic and creep compliances should be modeled separately. Elastic compliance decreases due to physical aging and approaches to a steady state value. This can be modeled by an exponential function. On the other hand, the momentary creep compliance can be modeled by a power law. For long-term physical aging, the momentary creep compliance model would under-estimate the physical aging effect and an effective time must be used to replace the creep time in the momentary creep compliance model for more accurate predictions.

An effective creep compliance model was shown to be able to characterize physical aging in orthotropic composites. By using a one-parameter creep potential function, momentary creep compliances for different fiber orientations can be collapsed into a single master curve from which creep curves in any direction in the composite can be derived for any aging time.

Moisture and temperature can relax the elastic and creep compliances throughout the entire aging period. By choosing room temperature and 0 % moisture content as reference, a moisture-temperature equivalence in physical aging can be established for elastic and creep compliances. This equivalence enables us to interchange the effects of moisture and temperature on physical aging in polymeric composites.

The application of laminate theory to characterize physical aging in elastic compliance of composite laminates has been verified.

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1. Struik, L. C. E., *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier Scientific Pubilshing Company, New York, 1978.

2. Hu, Huiwen and Sun, C. T., "Characterizing Physical Aging on Polymeric Composites," *Proceedings of the 14th Technical Conference, American Society for Composites*, Dayton, Ohio, September 27-29, 1999, pp. 209-219.

3. Hu, Huiwen and Sun, C. T., "The Characterization of Physical Aging in Polymeric Composites," *Composites Science and Technology* (60), 2000, pp. 2693-2698.

4. Hu, Huiwen and Sun, C. T., "Moisture Effect on Physical Aging in Polymeric Composites," Proceedings of *Proceedings of the 15th Technical Conference, American Society for Composites*, Texas A&M University, September 24-27, 2000, pp. 548-556.

5. Hu, Huiwen and Sun, C. T., "Moisture-temperature Equivalence in Physical Aging of Polymeric Composites," *42nd AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference and Exhibit* (AIAA-2001-1287), Seattle, April 16-19, 2001, pp.1-7.

# PUBLICATIONS

1. Hu, Huiwen and Sun, C. T., "Characterizing Physical Aging on Polymeric Composites," *Proceedings of the 14th Technical Conference, American Society for Composites*, Dayton, Ohio, September 27-29, 1999, pp. 209-219.

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4. Hu, Huiwen and Sun, C. T., "Moisture-Temperature Equivalence in Physical Aging of Polymeric Composites," *42nd AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference and Exhibit* (AIAA-2001-1287), Seattle, April 16-19, 2001, pp.1-7.

5. Hu, Huiwen and Sun, C. T., "Moisture-Temperature Equivalence in Physical Aging of Polymeric Composites," submitted to AIAA Journal for publication.

## GRADUATE STUDENT SUPPORTED

Huiwen Hu, PhD August 2001, School of Aeronautics and Astronautics, Purdue University, West Lafayette, Indiana.

Figure 1. Elastic compliances of 90° specimen at 104 ℃
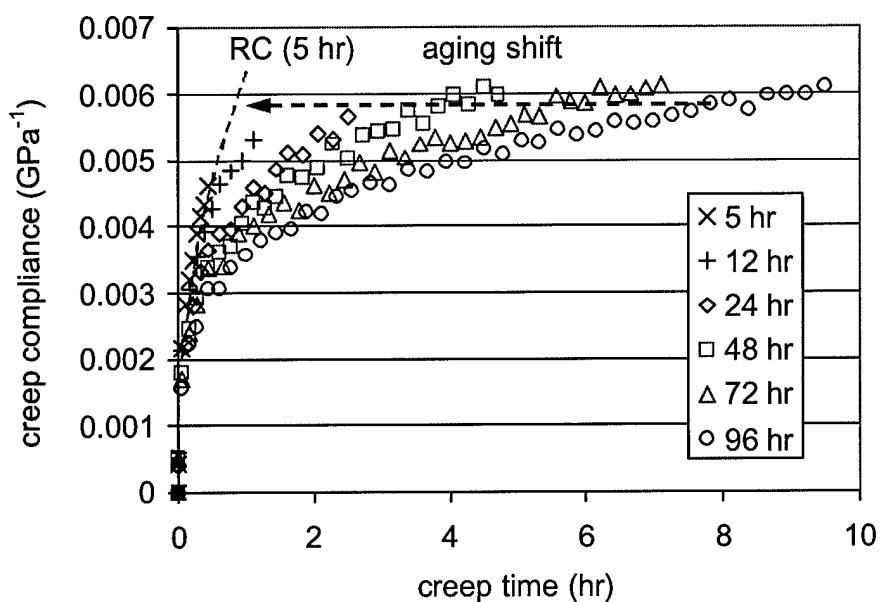


Figure 2. Momentary creep compliances of 90° specimen at 104 ℃

Figure 1. Elastic compliances of 90° specimen at 104 °C
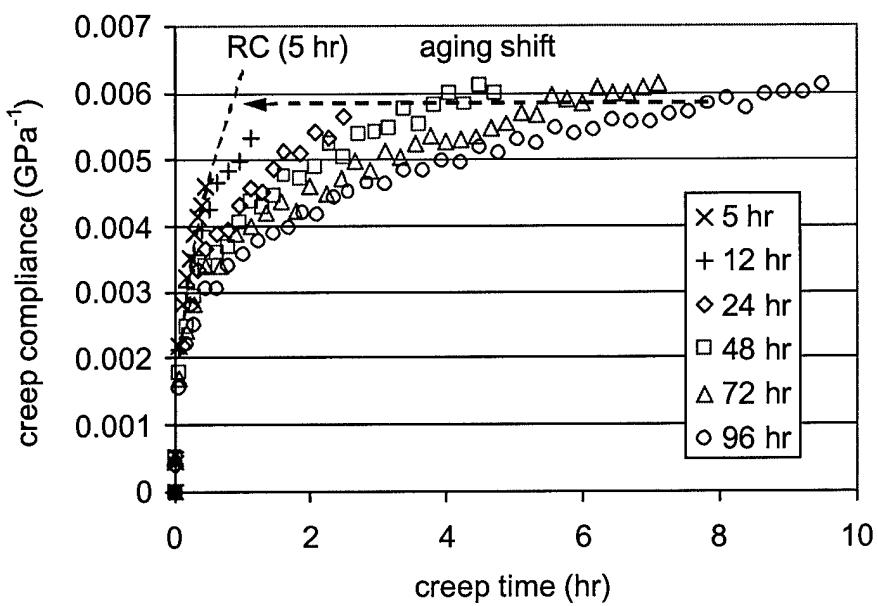


Figure 2. Momentary creep compliances of 90° specimen at 104 °C
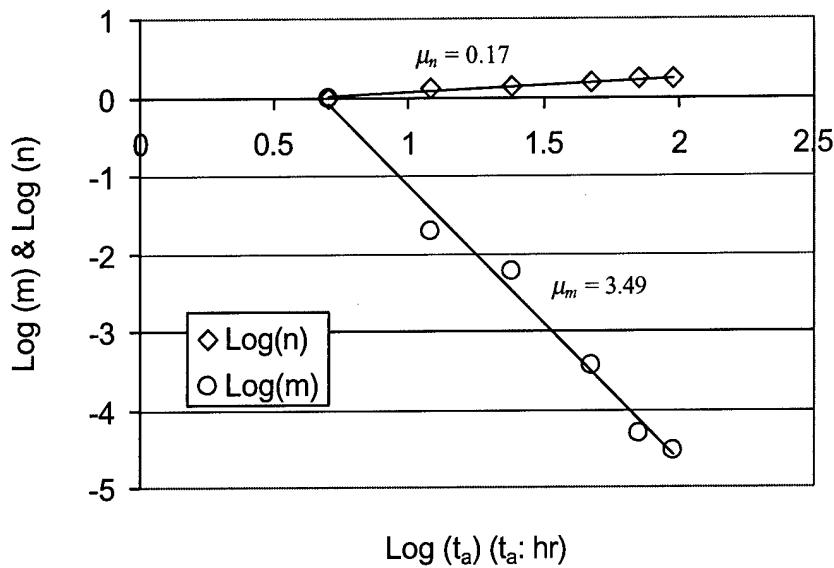
Figure 3.  Shift factors and shift rates of curves in Figure 2
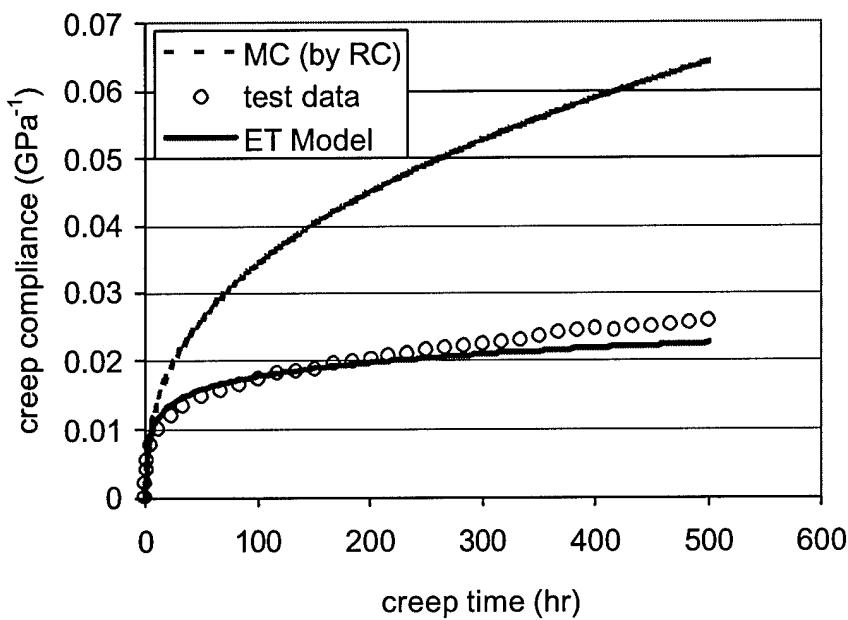


Figure 4.  Long-term creep compliance of 45° specimen with 5-hr initial aging

10
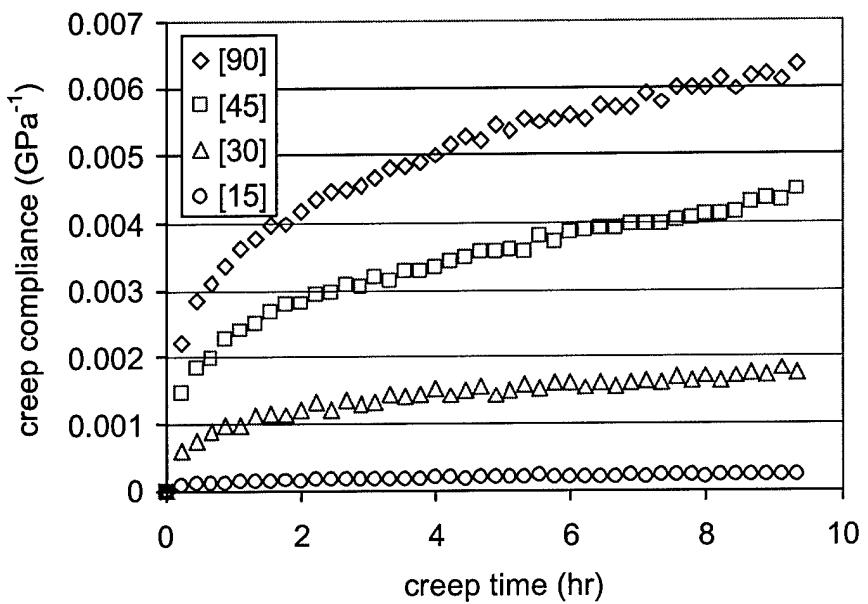
Figure 5. Momentary creep compliances of 96-hr aging
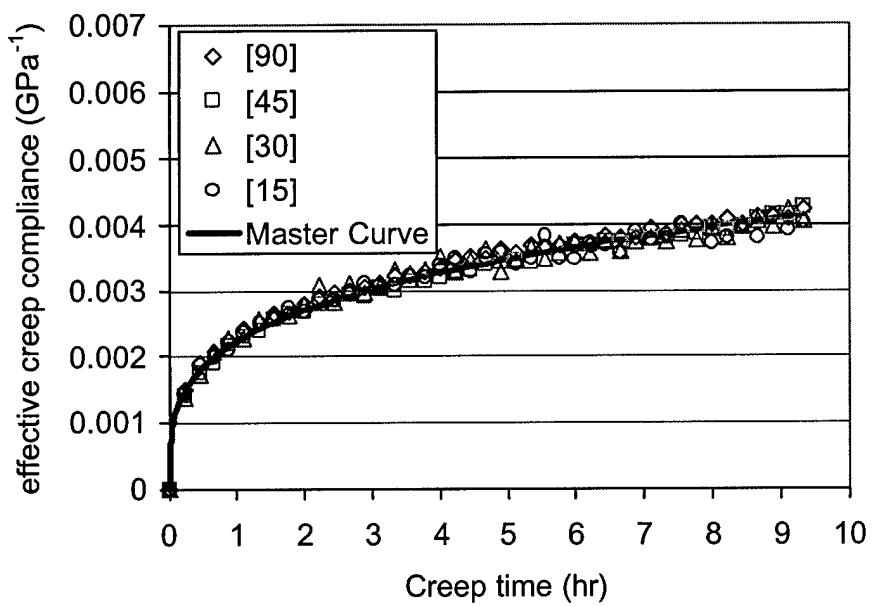


Figure 6. Effective momentary creep compliances and master curve of 96-hr aging ($a_{66} = 0.95$)
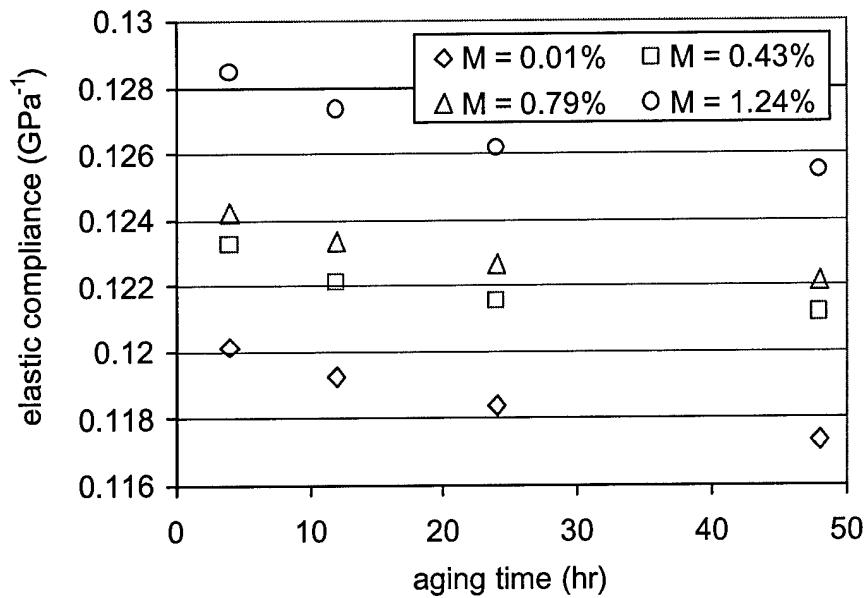
Figure 7 Elastic compliances of 90° specimen with moisture contents at 23 °C



$$a_M^e = 0.053M + 1$$
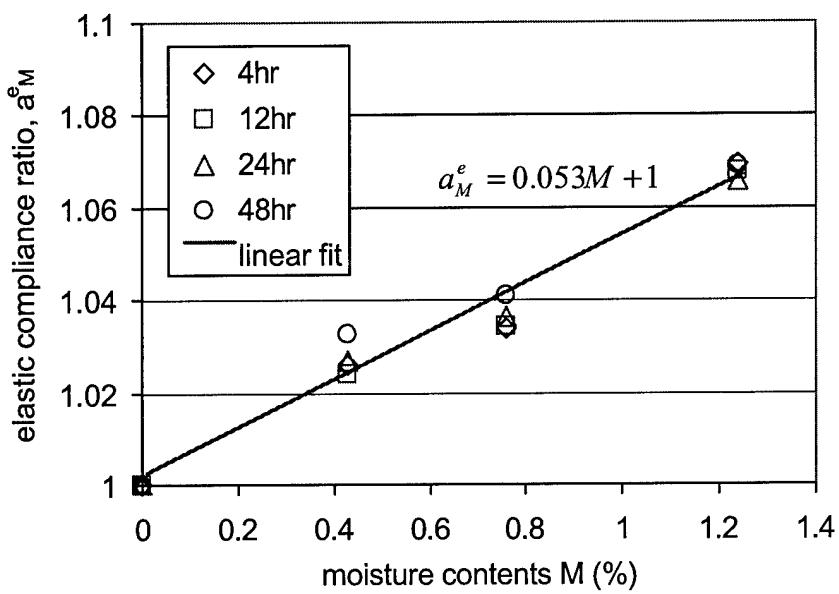
Figure 8 Elastic compliance ratio of 90° specimen at 23 °C
versus moisture content
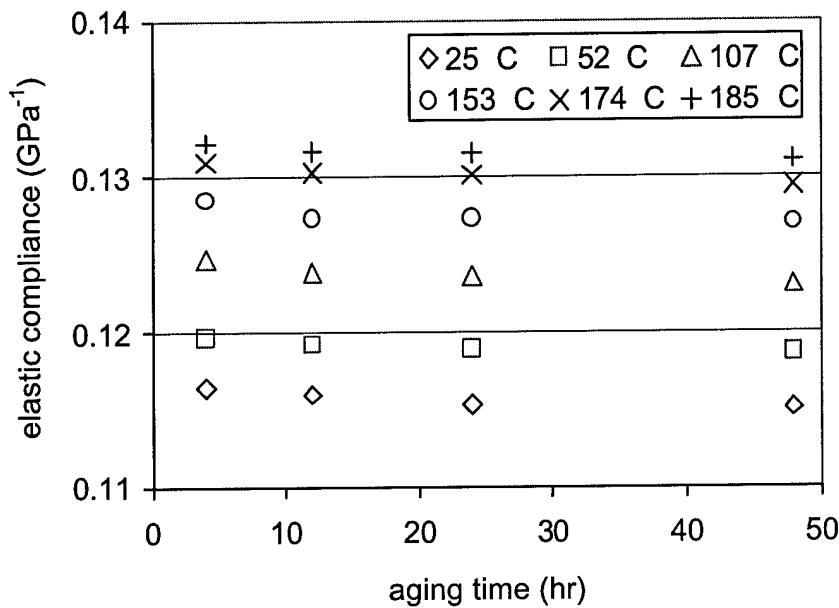
Figure 9 Elastic compliances of 90° specimen at isothermal conditions
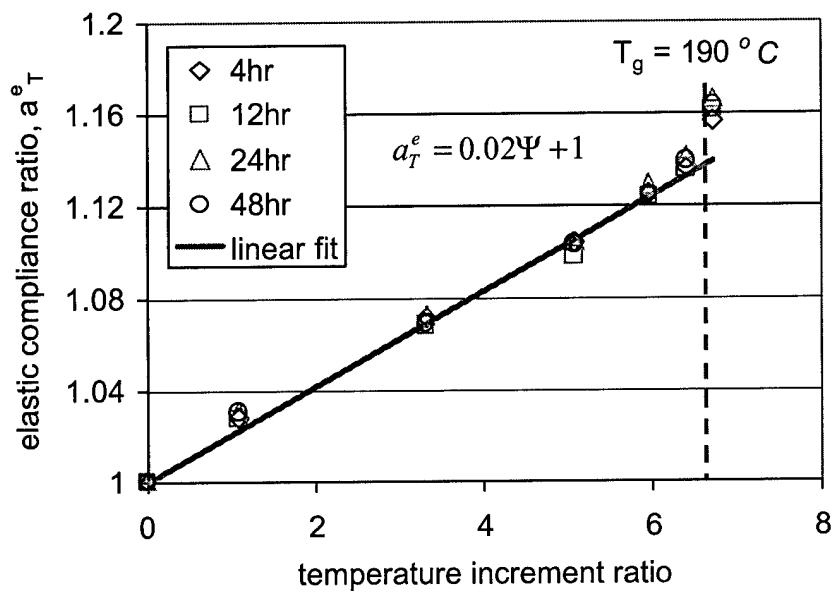


Figure 10 Elastic compliance ratio of 90° specimen versus temperature increment ratio
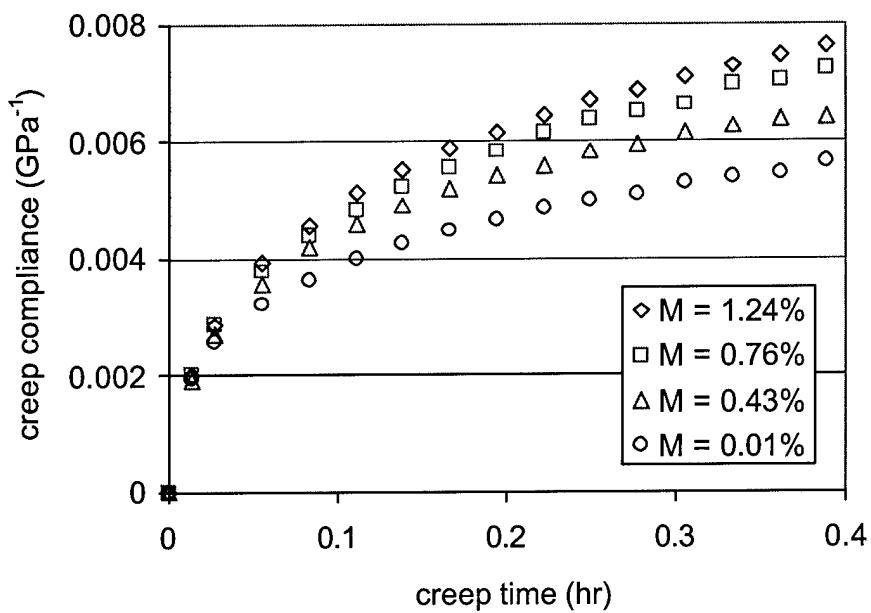
Figure 11 Creep compliances of 90° specimen with moisture contents after 4-hr aging
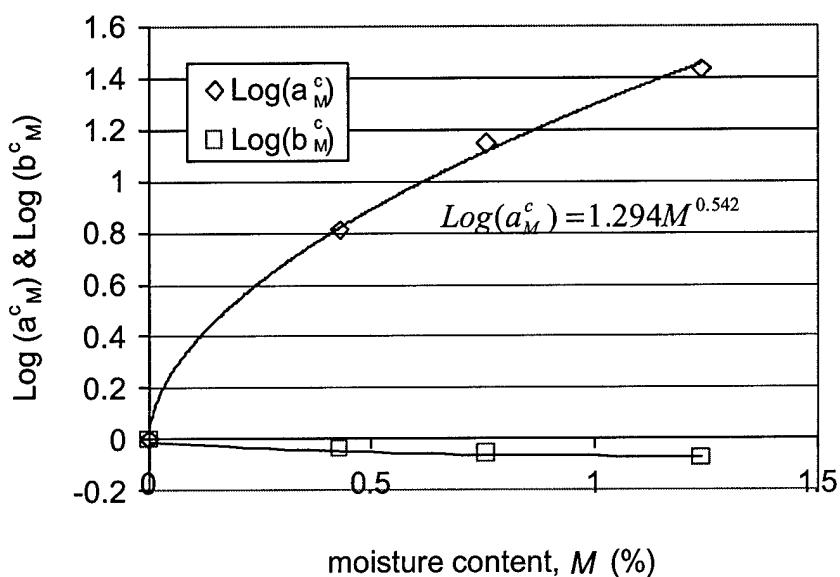


Figure 12 Logarithmic shift factors versus moisture contents in Figure 11
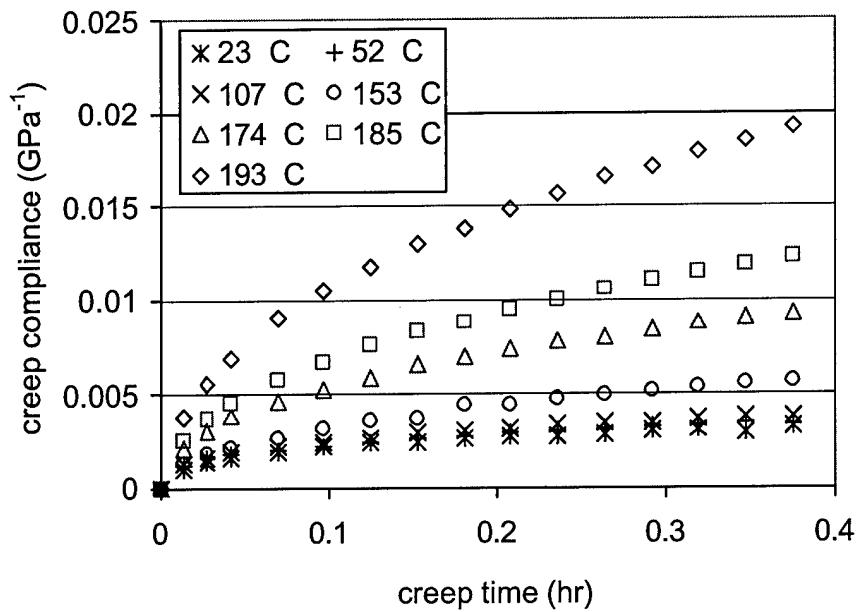
Figure 13 creep compliances of 90° specimen at constant temperatures after 4-hr aging



$$Log(a_T^c) = 1.294\Psi^{0.542}$$
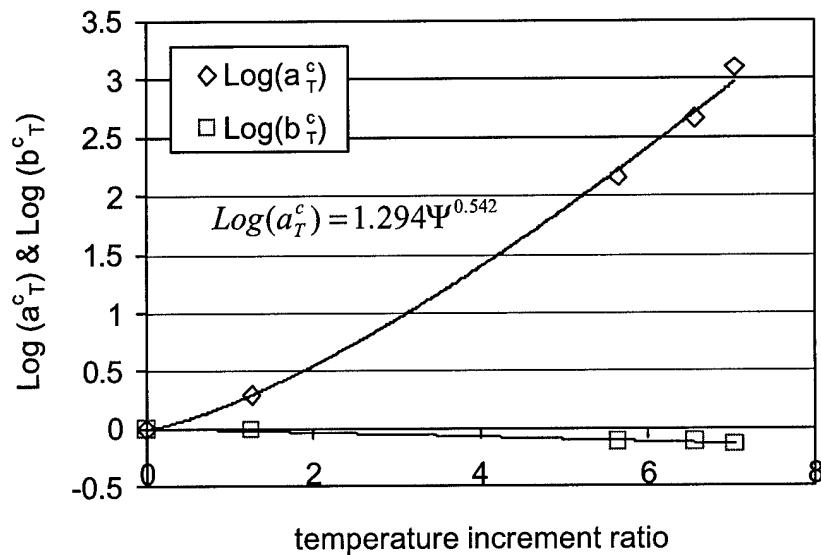
Figure 14 Logarithmic shift factors versus temperature increment ratio in Figure 13
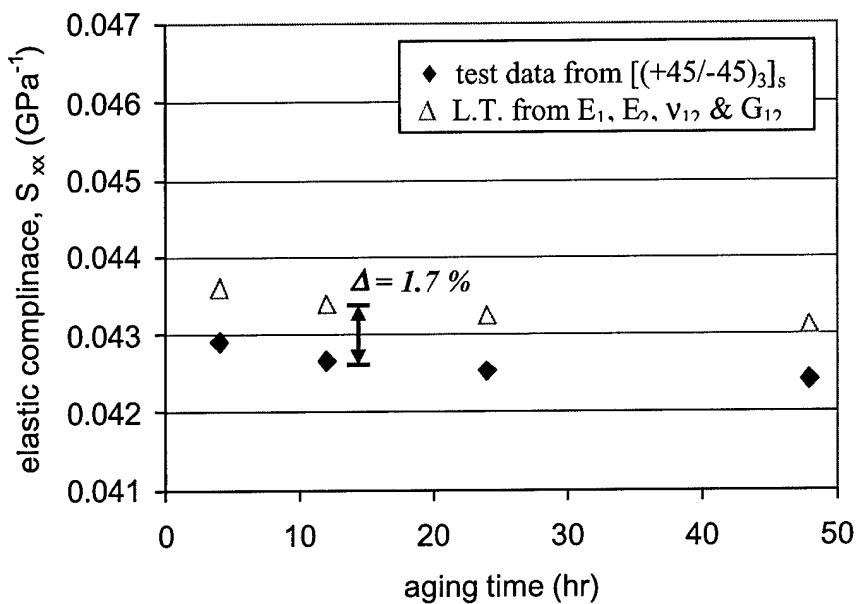
Figure 15 Elastic compliance of laminate [(+45/-45)₃]ₛ at 107°C versus aging time
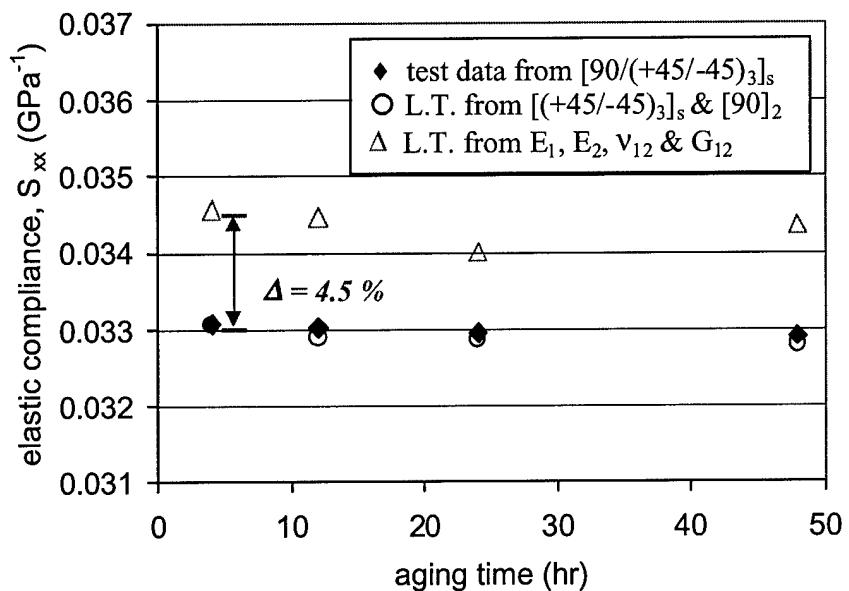


Figure 16 Elastic compliance of laminate [90/(+45/-45)₃]ₛ at 107°C versus aging time